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A STUDY OF INFRA-RED SENSITIVE PHOSPHORS

THOMAS CHAPPELL ALDRIDGE

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A STUDY OF
INFRA-RED SENSITIVE PHOSPHORS

THOMAS CHAPPELL ALDRIDGE

A STUDY OF
INFRA-RED SENSITIVE PHOSPHORS

by

THOMAS CHAPPELL ALDRIDGE
" "
Captain, United States Army

Submitted in partial fulfillment
of the requirements
for the degree of
MASTER OF SCIENCE
IN
PHYSICS

United States Naval Postgraduate School
Monterey, California

1954

Thesis

A 37

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IN

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ACKNOWLEDGMENTS

The writer wishes to thank Professors William P. Cunningham and Sydney H. Kalmbach of the United States Naval Postgraduate School for their assistance in the preparation of this paper and also to thank Mrs. T. C. Aldridge for her assistance in the preparation of the figures.



PREFACE

Many infra-red sensitive phosphors are in use today although the development of the infra-red phosphors is considered by many as not having advanced beyond its infancy stage. The use of the existing phosphors may be continued, however, without further knowledge of why these phosphors are affected by infra-red radiation as they are. But for real progress or advancement in this field, a more complete theory must be developed. Of course, some basis for new theory comes from "accidents" happening during the utilization of these phosphor devices, but these events happen rather infrequently. For steady and sure progress, we must still rely on the proven system of a definitely oriented program of basic research.

We shall discuss the processes for luminescent energy storage, which is an absolute prerequisite for phosphorescence, the physical means of attaining storage, that is, how trapping is accomplished, and lastly, how infra-red light stimulates the release of this energy in phosphorescence and in dissipation (quenching). Until we have a more exact comprehension of the above phenomena, the technical utilization of the infra-red phosphors is most severely limited.

This paper is a brief survey of what is known and what has been done, generally toward the development of the infra-red sensitive phosphors.

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I. INTRODUCTION

The advancement in the field of luminescence of solids has been slow. The biggest reason for this tedious movement is most likely because of the hybrid nature of the field itself. It includes major portions in such fields as Chemistry (for materials used), Crystallography and Geometry (for lattice and structure effects), and Physics (for the energy involved). And naturally, men qualified in all these fields are not as numerous as those in any one of them. However, during World War II, there was much done in the practical aspect of the utilization of the infra-red phosphors and much interest was created, a vital ingredient necessary for any appreciable scientific advancement. Even though the theories have not been changed, we realize the necessity for some revisions.

Attempts are made here to interweave correlations and interpretations where they exist and to bring out some of the later practical developments.

II. GENERAL CONCEPTS

Luminescence⁽¹⁾⁽²⁾ is a general term which includes the many phenomena involving the absorption of energy by a substance and its re-emission as visible or near-visible radiation. The emission during the excitation is referred to as fluorescence, that which persists after excitation is known as phosphorescence. To provide a line of demarkation between the two types of radiation, the limit of fluorescence is fixed at 10^{-8} seconds after excitation has ceased, this being the order of the relaxation time of an isolated gaseous ion.

Phosphorescence is not limited to solids. However, phosphorescence of long decay duration is usually confined to crystalline solids of inorganic constitution whose luminescence is due to activation by traces of impurities. This phenomenon will be explained in detail later. Such solids require special preparation, the inclusion of the impurities being affected by the treatment with heat. As an example, zinc sulfide activated by copper shows a green glow lasting about an hour. Such solids are called phosphors.

There is some interest in solids which show luminescence in the pure state although their practical use is restricted. Studies made by Raman show that luminescence is characteristic of even very pure diamond⁽³⁾. However, such phosphors have not been found to be sensitive to infra-red illumination. And further, these pure state phosphors have not been found to have any practical value other than their contribution to the theories evolving from the study of Solid State Physics, in particular, the idea that luminescence is a result of the state of physical structure or lattice configuration.

All phosphors found, having marked sensitivity to infra-red stimulation and also enough practicality to have been investigated, have belonged to the impurity activated classes. The predominant ones, discussed later,



are the zinc and alkaline earth sulfides. But first, let us look at the principles involved in the phenomenon of luminescence.

A. PRINCIPLES OF LUMINESCENCE

Luminescent emission (visible and near-visible radiation) by a substance will depend upon the efficiency with which the absorbed energy can be protected from dissipation. Further, if energy absorbed is not emitted at the same specific point in the material, then there must be some means by which the energy can be transferred or transported, without appreciable loss, from the place of absorption to the centers in which emission occurs. These energy-release points will be referred to as luminescence centers. In these centers the electron transitions responsible for the luminescence emission can take place with a minimum of disturbance from the environment. Any such disturbance will increase the probability of a non-radiative dissipation which we shall call quenching. The goal is, of course, to produce a perfect infrared sensitive phosphor, that is, to make a phosphor that will not be affected by environment. In this case there would be no effect of quenching and the phosphor would be able to store luminescent energy for an indefinite period.

L. THE GROWTH OF KNOWLEDGE OF LUMINESCENCE THROUGH SOLID STATE PHYSICS⁽⁴⁾⁽⁵⁾

The background for this study seems to have had its beginning in the study of solid state physics, in particular, the study of semi-conductors. The knowledge of the electrical conducting properties of semi-conductors seemed to be the first step in the evolution. For example, zinc oxide that has been formed at low temperature is a pure white substance having no appreciable electronic conductivity. After being heated to a high temperature, it develops a brownish hue and becomes a conductor at room temperature.

P. Drude was the first known to suggest that the electrical and thermal properties of metals might be correlated by assuming that metals contain free electrons in thermal equilibrium with the atoms of the solid. He also



introduced the concept of a mean free path for collision of free electrons.

Another related concept is photoconductivity. Measurements on the photoconductivity of natural single crystals and artificially prepared powders of a zinc sulfide phosphor can be of assistance in the interpretation of the basic theories of luminescence. Although the impurity content of the single crystals was not discussed by the experimenters, we shall assume that the composition of crystals and powders is similar, since the photoconducting properties of both are very nearly alike. The photoconducting powders were usually prepared by heating pure zinc sulfide either alone or in the presence of small quantities of salts of the other metals such as copper, manganese, or silver. It is believed that small quantities of the neutral metal atoms enter interstitial positions in the lattice as a result of the heating process and provide centers that may be ionized by the conductivity-inducing radiation in the near-ultra-violet. The position of the spectral sensitivity curve is dependent upon the kinds of interstitial atom present. In the pure state, it was explained as imperfections in the lattice or structure that caused the same type of effect as that caused by a foreign atom. Many of the photoconducting zinc sulfides, such as the pure heated materials and those activated by means of copper, silver, or manganese, luminesce brightly when excited with radiation lying in the region wherein photoconductivity occurs.

The primary current, in sufficiently thin crystals, saturates. From calculations based on this, it is determined that the density of trapping centers is very low compared to the density of interstitial atoms.

The trapped electrons may be temporarily released by heating the crystal (quenching-dissipation by heat) or by illumination with infra-red light at any temperature. This freeing is made evident by the appearance of conductivity. Hence, if a crystal that has been previously illuminated with ultra-violet light is continuously illuminated with infra-red light or is kept

sufficiently warm, the electrons that are continuously being freed from the trapping centers should eventually recombine with the ionized interstitial atoms and the conductivity should gradually decrease. Due to the peculiarity or efficiency of the particular phosphor the emission of light in each case is different. A comparison of the two processes on a similar phosphor will be given later.

Reimann⁽⁶⁾ observed on a specimen of zinc sulfide that the resistivity of a crystal illuminated by infra-red light, increased linearly with time if the specimen was kept at liquid air temperature and initially excited with ultra-violet light.

The equation of the rate at which electrons and interstitial ions recombine (assumed to be proportional to the number of each) agreed very nearly with the experimental equation for the decay of the luminescence of zinc sulfide. However, this experimental data must not be taken at times too near the initial time of excitation, this time being a fraction of a second.

Ionic conductivity of solids is closely connected with the type of lattice imperfections that occur in semi-conductors. Two such types are interstitial positions and vacant sites. An ion may move through a crystal utilizing these two types of lattice imperfections as "stepping stones", either or both of which may be used in this ionic conductivity.

It is surmised then that stimulating excitation liberates electrons from neutral interstitial atoms of the impurity metal, or of zinc in the pure phosphor, and that light is emitted when the electron and interstitial ion recombine, the color of the emitted light depending, of course, upon the interstitial atom that does the emitting. With the freed electron being trapped and not immediately re-combined, the crystal is phosphorescent.

The wave length of the emitted light radiation is always longer than that of the exciting radiation. The emission band is broad at room temperature and becomes narrower as temperature is lowered and usually consists of a single sharp line with several weak satellites at extremely low temperature. This phenomenon is due to the fact that the vibrational modes of the crystal are receiving less stimulation at this temperature. So there seems to be agreement with the principle that luminescence is caused by absorption and emission of energy by electrons.



III. MODELS FOR LUMINESCENT MATERIALS

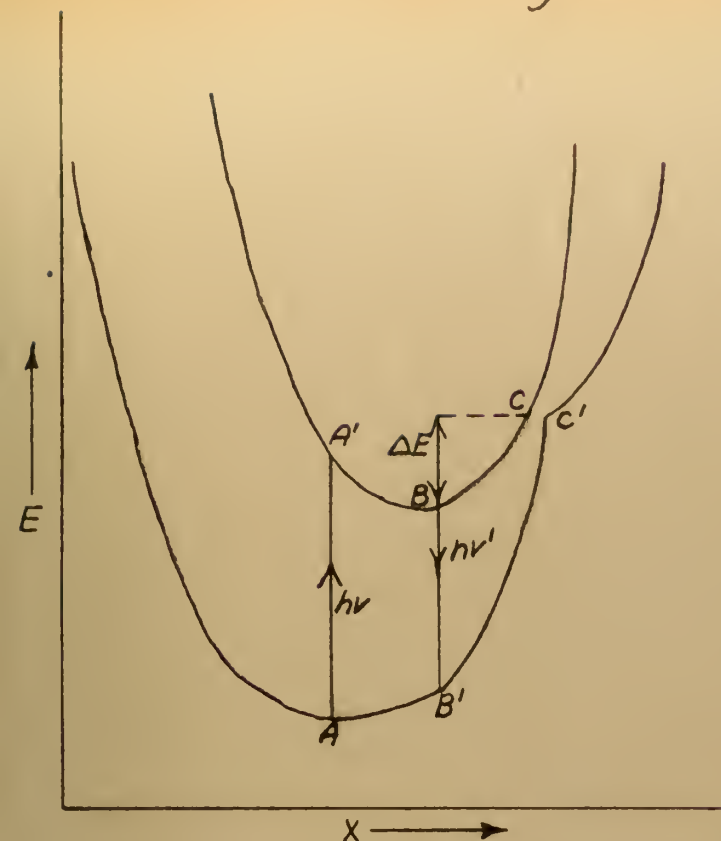
Sometimes a schematic model is helpful in comprehending the principles of a system. Let us first consider a model proposed for any luminescent material. Diagrams of potential energy versus a position coordinate have been applied with success to problems of molecular spectra and rates of chemical reactions. In such applications the position coordinate can usually be precisely specified as an inter-atomic distance. To describe completely the atomic rearrangements involved in electronic processes in solids would require energy contours in a configuration space having three times as many coordinates as there are particles involved. In describing the transitions and rearrangements occurring in luminescent phenomena, a useful simplification is to define a "center" as the excited atom plus the group of neighboring atoms participating in the rate processes, and then specifying to the first approximation the coordinates of the center by an average configuration coordinate. Such a model is Figure 1.

A. MODELS IN GENERAL

As the stable configuration of constituents of the lattice in the neighborhood of the excited center will be different for both states, the minima of the two curves do not correspond. Normal optical transitions between the ground state and the excited state are restricted by the Franck-Condon principle and occur without changing the atomic configuration (vertical jumps). Adaptation of the position of the surrounding atoms to the changed situation occurs only after the electronic transition has taken place. The system moves downwards in the mold of the curve and the excess energy is dissipated as heat. When energy ΔE is added, the system moves from B to C. The transition between the curves from C to C' takes place nearly without change of energy. This probability is nearly independent of the temperature, de-



Fig. 1

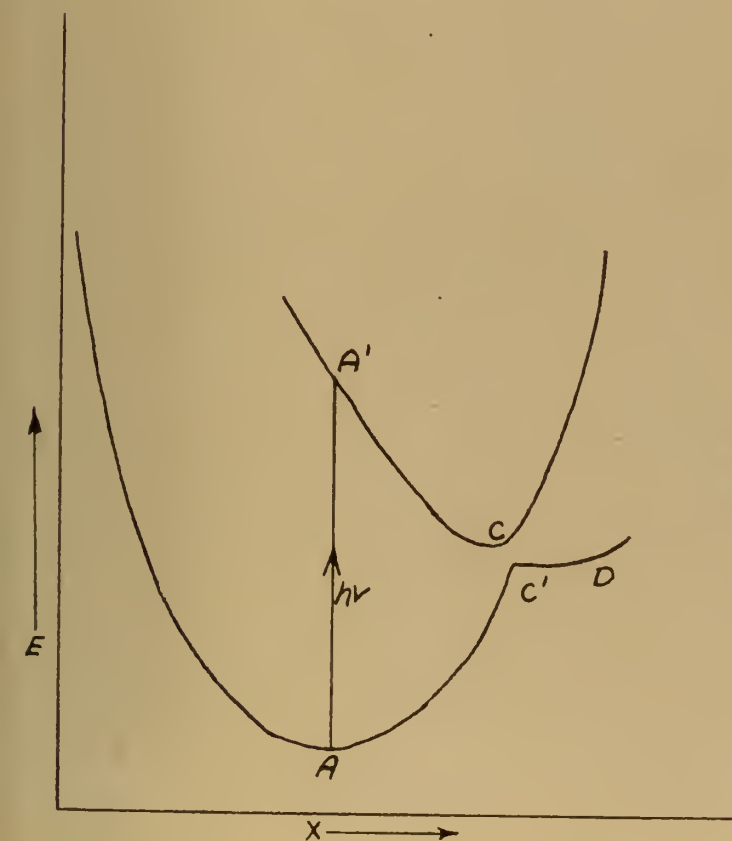


(a) Energy-configuration conditions for luminescence in an atomic center after energy absorption.

AA' , absorption act;

BB' , luminescence transition;

CC' , radiationless transition.



(b). Energy-configuration conditions for radiationless dissipation of absorbed energy in an atomic center.

AA' , absorption act;

CC' , radiationless transition;

D , metastable state.

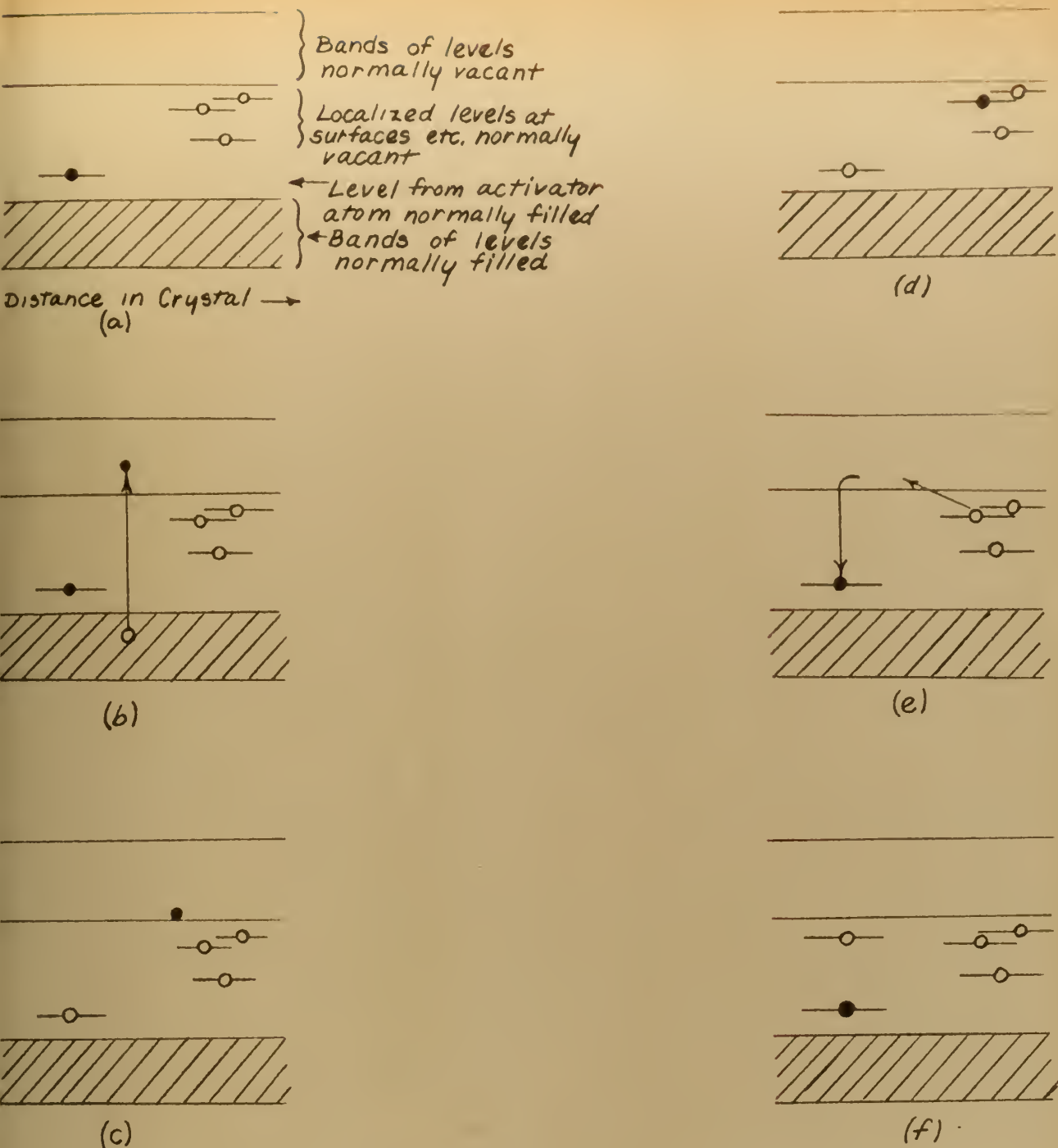
pending upon the coupling which exists between the electronic states and the vibrations; it is small when the coupling is small. This is probably realized in excited systems which are well screened off from the surroundings, for example as in the rare earths. The movement from C' to A is dependent upon the interaction of the localized vibrator with the surrounding vibrators as well as upon the temperature. Figure 1 (1), of course, since it has no visible component is a pure absorber.

B. MODELS FOR INFRARED SENSITIVE PHOSPHORS

The luminescence process consists of three stages: (1) the absorption of energy, (2) the transport and storage of absorbed energy, and (3) the release of the stored energy and emission of luminescence. Therefore, we must have a model that will explain these three principal stages. Our diagram allows the electrons to be assigned to an energy band that is in turn related at least qualitatively, to the energy of an electron at infinity. Symbols can represent the energy levels of the interstitial activator atoms, the trapping levels, and any other localized energy levels filled or unfilled. The diagram is merely a device to substitute a picture for many words, to give us something to point at, and to give physicists something to argue about. Such a model is shown in Figure 2.

Electrons may be excited from the uppermost filled energy band levels of the crystal into the empty conduction band levels by the primary absorption process or they may be raised from the ground states in the luminescence centers due to the activating impurity. Either process will result in the emptying of luminescence centers by direct or indirect removal of electrons if the positive holes created in the full band can capture electrons from luminescence centers.

Fig. 2



(a). Distribution of energy levels for electrons in an impure insulating crystal such as ZnS-Cu. Excitation raises an electron from the lower filled band to a level in the upper band (b). Its place is taken by an electron from an activator level (c) as the excited electron itself settles to the lowest level in the conduction band. The excited electron is trapped in a level associated with the lattice irregularity (d) and returns to the activator level, with emission of light, only after it has been re-excited to the upper band (e). (f) shows the model with the addition of a second level for the other activator atom.

Electrons raised into the conduction band may then either recombine with empty luminescence centers or be captured by the electron traps present in the phosphors. Phosphorescence will then be due to the subsequent release of the trapped electrons and their return to luminescence centers to cause emission and will be governed by the mean time spent in the trap by the captured electron. The mean time " t " is the reciprocal of the probability of escape " p " and is dependent on the "depth" of the electron trap " E " and the temperature " T " according to the expression $p = 1/t = s \exp(-E/kT)$. s being the order of 10^3 second^{-1} and k being Boltzman's constant⁽⁷⁾⁽³⁾⁽⁹⁾. Further discussion of the effect of trap depths as related to the decay characteristics will be given later.

But to investigate the feasibility of the simple band energy model diagrams, based on the energy-band theory of solids, let us look at the observations made and see if these observations are capable of agreement with the sulfide and silicate phosphors.

1. The Sulfide Model⁽³⁾

a. The space density of the trapping states and their distribution in the energy of trapping (energy required for raising an electron from one of them to the upper conduction band) may be expected to vary widely among different samples, depending on the details of mixing, heating, and the like. A corresponding diversity in the observations is evident when one regards, for example, the multifarious empirical laws proposed by different investigators to fit their own data on decay. This is not in itself conclusive, but it does furnish some basis for development of an acceptable theory for the decay of emission from infra-red sensitive phosphors.

b. The color of the emitted light and the course of decay should

be independent of the mode of excitation. This is usually found to be the case.

c. The detailed course of the decay curve (log of the brightness plotted against the time of decay-using arbitrary scales for the brightness) at room temperature will obviously depend on the detailed distribution of the trapping states, but its general shape can be found by a single approximate analysis. This calculation shows that invariably the decay should begin at a finite rate from the level of brightness during excitation, that the semi-log plot should be concave upward, and that its initial steepness should be greater, the greater the initial brightness. These are just three generalizations that emerge from the vast quantity of data on decay of sulfides, when the variations among individual samples are overlooked.

d. The efficiency should be high, since the model includes automatic transport of excitation energy from any point in the lattice to the neighborhood of an activator atom where it is available for luminescence. The measured efficiencies, for comparison, are of the order of fifty per cent (watts per watt) in ultra-violet excitation, of the order of five to ten per cent in electron bombardment at high voltages, and reportedly in a case of alpha-particle bombardment as high as eighty per cent.

e. At elevated temperatures the decay should obviously be more rapid. This is also generally a fact.

f. The sulfides should fluoresce at low temperatures. Whether or not they show a visible low phosphorescence will depend upon the density of the trapping states near the upper conduction band. Actually the sulfides as a group fluoresce and phosphoresce in liquid air quite brightly.

Also at low temperatures there should be a pronounced storage of light recoverable upon heating - this is, of course, a well-known phenomena.



g. Suppose the decay curve of a sample which has been excited to equilibrium with a source of low intensity is taken as a standard, and is compared with the decay of the same sample brought to the same initial brightness by brief excitation with a more intense source. In this brief excitation the upper trapping states will have come more nearly to the equilibrium filling than the lower trapping states, and hence the decay curve will initially be steeper than the standard curve and will increasingly fall below the standard during decay.

If, on the other hand, suppose that the standard low level of initial brightness is reached by decay after excitation to equilibrium with an intense source, then during the decay the upper trapping states will empty more rapidly and by the time the observation begins the upper trapping states will have been depleted while the lower trapping states retain almost their entire initial complement of electrons. The remaining part of this decay curve will therefore be initially less steep than the standard curve and will increasingly lie above the standard curve during decay. These predictions are easily tested and are found to be true for the sulfide phosphors as a group.

h. Photoconductivity, which is high during excitation and "phosphorescent"⁽⁶⁾⁽¹⁰⁾ thereafter, appears readily as a net drift of the loosely trapped electrons in an applied electric field. The types of currents during the excitation and "phosphorescent" periods are referred to as the primary and secondary currents respectively. The primary current is independent of the time of excitation but is proportional to the intensity of radiation and is affected by the applied potential. The secondary current is, initially at least, dependent upon the duration of the illumination, the upper limit being reached when the primary current has reached saturation. The secondary current decreases at a rate similar to the rate of



decrease of phosphorescence, hence the term "phosphorescent" used above.

i. The sulfide model is consistent with the existence of saturation effects⁽¹¹⁾, commonly and plausibly attributed to the fact that as the intensity of excitation is increased, the number of centers (here, impurity states) which are instantaneously excited and so are not available for excitation becomes finally comparable with the total number of centers.

j. Excitation, in the model, is essentially a one-stage process, the time required for condition of Figure 2(d) being supposedly negligible in comparison with the time between (d) and (e). It follows that the brightness during excitation should increase smoothly from zero up to its equilibrium value. This behavior appears in a few cases where build-up curves have been measured⁽¹²⁾. If the excitation were a two-stage process, the electrons being excited to an upper state, decaying into an intermediate state, and thence to the ground state, with emission of luminescence, a simple analysis would show that the build-up curve should have a point of inflection, and that after a sufficiently brief excitation, the brightness should increase for a time. Neither of these effects have been reported (the second could make sulfide screens useless for television purposes); so it is fair to say that the model is consistent with the observations on kinetics of excitation.

k. The familiar effect of infra-red radiation in hastening the decay of sulfides is clearly due to the excitation, by infra-red quanta, of electrons from the low lying trapping states to the upper trapping states or to the upper band. This interpretation is supported by the three easily demonstrated facts: (1) The infra-red is relatively ineffective if the irradiation follows too closely after excitation. It is necessary to wait until the electrons in the upper trapping states, which are readily freed

by temperature excitation, have become so few that the brightness is limited by the rate of excitation from the low lying levels, (2), when irradiation with infra-red of constant intensity is begun, the brightness of the decaying sample rises gradually and goes through a maximum. This build-up period is to be expected, since the irradiation requires time to bring about a new quasi-equilibrium distribution of trapped electrons in which the upper states are more densely populated than they should be in the absence of infra-red, and (3) correspondingly, after the irradiation is stopped time is required for the electrons to sink back toward a new quasi-equilibrium distribution. During this period the sample remains abnormally bright - there is a "phosphorescence" of the acceleration action of the infra-red. In other words, the effect of the radiation does not end with the cessation of exciting radiation but slowly diminishes with time.

2. Silicate Phosphor Model

Silicate phosphors differ from the sulfides in their decay characteristics. During the first few milliseconds (10-100) of the decay, the brightness decreases exponentially at a rate which varies among the different types of silicates, but does not vary among different samples of the same type. In addition, the rate is independent of the nature of the energy, the rate of arrival of the exciting particles, the duration of the excitation, and the temperature, if it is not too high. Later the brightness declines much less rapidly, and the shape of the curve in this later period does vary from sample to sample and on the other parameters listed. That is, only after the initial decay, does the silicate resemble that of the sulfides.

The proposed silicate phosphor model (figure 2, f) differs in that there are two localized (impurity) states at different levels with only the lower one being filled normally. The gap between the two bands being approximately one electron volt larger in the silicates, thus the existence of two



activator states instead of one is not implausible. A quantum of luminous light results from the transition of an electron from the upper to the lower of these two levels; this transition is assumed to be radioactive in character, that is, little affected by external parameters, and to require an average time of the order of ten microseconds. Excitation and decay then proceed nearly as the sulfides, the essential difference being that an excited electron has high probability of being captured by one of the upper impurity levels rather than a trapping state. It is further necessary to assume that an upper impurity level is accessible to electrons only if the associated lower level is vacant. The decay rate being at first limited by the rate of transition between the first two impurity states and then by the rate of excitation of trapped electrons up to the conduction band.

Obviously this could account for the decay curve of the two phases described⁽¹³⁾.

The silicates at the temperature of liquid air do not exhibit the persistent component of decay, and after excitation in liquid air they have to be warmed to higher temperatures than do the sulfides before they yield the stored light at comparable rate. Photoconductivity in the silicates is several orders of magnitude lower than the sulfides. The observations are consistent in indicating that, with the silicates, the trapping states in the region of energy just below the upper band are not as dense as the sulfides.

The silicates, as compared with the sulfides, are only slightly affected by irradiation with a continuous spectrum of infra-red light. As a silicate warms up after excitation in liquid air, its brightness goes through a succession of maxima and minima; sulfides in the same experiment usually go through a single broad maximum of brightness. This indicates that the trapping states in the silicates are more closely bunched about particular



energies-of-trapping than in the sulfides. A comprehensive discussion of the decay of phosphors is given by Ellickson⁽¹⁴⁾ and Meyer⁽¹⁵⁾.

M. E. Wise⁽¹⁶⁾ attempts to show, however, that many recent experiments provide good reason for doubting whether one can apply the accepted band-theory at all to insulating crystals (semi-conductors or phosphors) in which the conductivity and luminescence are due to impurities.

Since in this short space all the various ideas concerning phosphorescence cannot be presented, we shall stick more closely to the most widely accepted theories of the phosphors more directly concerning the infra-red phenomena.



IV INFRA-RED RADIATION EFFECTS ON PHOSPHORS

A sample of the effect of the infra-red radiation on phosphors is given in Figure 3⁽¹⁷⁾. As it is seen, the infra-red effect is a secondary one. The phosphors must have received energy from another source to be in its excited state for luminescence to be a noticeable effect.

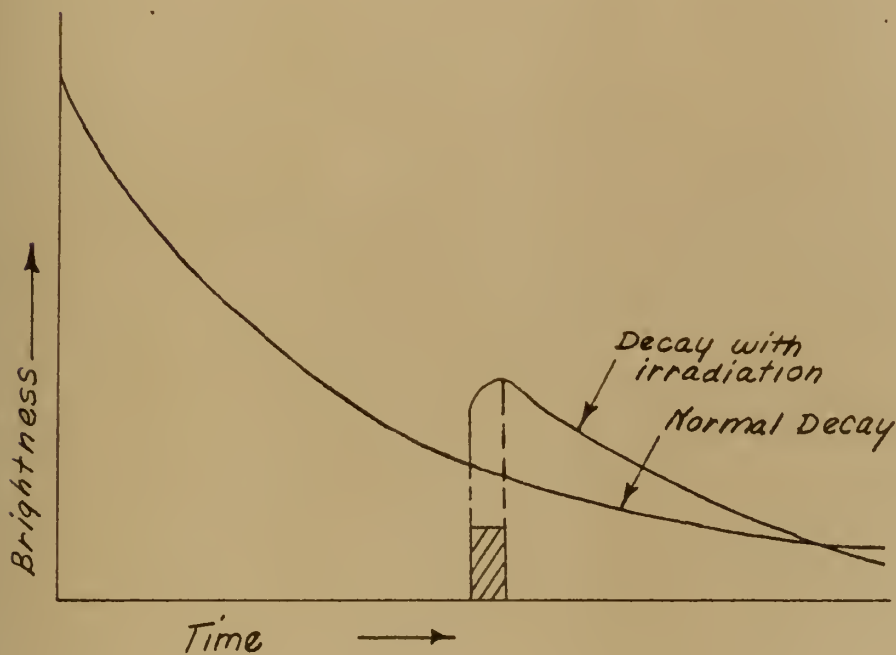
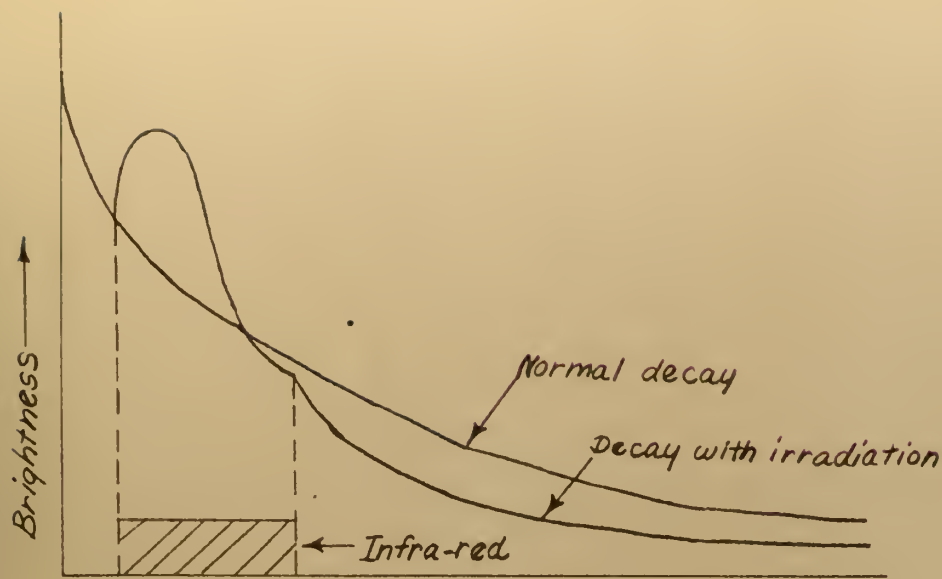
Phosphors which exhibit a decrease or increase of visible luminescence when exposed to infra-red radiation have been known to exist for a long time. Such visible luminescence must first be excited by radiation of a shorter wave length than the visible light emitted or by some other source, other than light, as this is inherent in the acceptance of Stoke's Law. That is, the emitted quantum is never greater than the absorbed quantum⁽¹⁸⁾⁽¹⁹⁾. Therefore to accept Stoke's Law for the normal process of luminescence, we must have a different explanation for the infra-red effect on phosphors.

Afterglow (luminescence continuing after the removal of the exciting radiation) may be quenched by infra-red radiation without further emission of visible light. On the other hand, the visible afterglow may be allowed to decrease, after which additional luminescence may be stimulated by exposure to infra-red radiation.⁽²⁰⁾

A. QUENCHING

First, let's take the quenching phenomena as it pertains to all phosphors. Quenching is any process that increases the probability of non-radiative dissipation of energy stored in the phosphor. Several theories have been proposed⁽¹⁾. Quenching was the first infra-red process investigated. Photographs were produced using this method. However, with the stimulating effects available, the negative type action was dropped for the positive type stimulating action. For example, a picture of a dark object

Fig. 3



(a). Continued exposure to low energy quanta reduces the supply of trapped electrons in a phosphorescing sulfide below its normal value, and the sample afterwards is abnormally dim. (b). Brief exposure to low energy quanta increases the number of trapped electrons in higher levels from which they can easily be freed by temperature excitation, and the sample afterwards is temporarily abnormally bright.

on a less dark background is more difficult to discern than a light object on a less light background.

The theory of Klasens-Schön⁽²¹⁾ states that quenching will occur if irradiation with the infra-red increases the rate of the migration of a "hole" to a quencher by liberating it from its original center. This is part of the explanation of the phenomenon of specific quenching of the phosphorescence by the "killers" iron, cobalt, nickel, manganese, and tantalum, while the fluorescence remains comparatively unaffected. The assumption was that the electron traps did not belong to particular centers but that the electrons released from traps may recombine with holes in centers of different kinds all over the lattice.

Möglich and Rompe⁽²²⁾ suggest that incorporation of activator atoms causes lattice defects. These distortions change the vibrational spectrum of the entire crystal, resulting in an increase in the probability of the dissipation process.

IV-B. STIMULATION

To understand the theory of infra-red stimulation, there are several facts that should be explained: (1) the sensitizing action of the secondary activators, (2) the difference between the stimulation and quenching processes, (3) the various forms of decay of stimulated emission with time, and (4) the variation of the infra-red effects with temperature.

Stimulation is the process by which the infra-red radiations instigate or accelerate the emission of visible light from a phosphor. But as before mentioned, the phosphor substance must have previously absorbed and stored the so-called phosphorescent energy for the infra-red irradiation to cause the emission of visible light. This was the principle used during World War II in developing instruments to get better "visibility" through fogs⁽²³⁾ and

through the darkness⁽²⁴⁾ of the nights.

Stimulation, then, is the result of some process of energy absorption of infra-red light by the phosphor substance. From the evidence of Ellickson⁽²⁵⁾ we conclude that infra-red or long wave length visible radiation does not affect the trapped electrons directly. Because if such a process existed, then at very low temperatures the stability of the electrons in the very shallow traps would cause the appearance of new absorption bands at much longer wave lengths than those which occur at room temperature. No such bands were found. Lenard assumed that absorption on infra-red radiation took place in special regions, the absorbed energy being subsequently transported or transferred to the phosphorescence storage centers which we have called electron traps⁽²⁶⁾⁽²⁷⁾⁽²⁸⁾. Kittel⁽⁵⁾ refers to these moving states of excitation as "excitons".

Somehow the sensitizing action is related to the presence of "secondary activators". Just in what manner do these secondary or auxiliary activators perform such an amazing feats. As yet no one, of course, knows.

It is likely that in some way the auxiliary activator prevents the non-radiative loss of the absorbed energy; this would account for its small effect at low temperatures when the non-radiative processes are less likely. Given later are some experimental data of the effects of some auxiliary activators and you can draw your own conclusion. So far not enough data are available to form any firm conclusion on this phase of the phosphor phenomena.

The sensitizing action of secondary activators has been reported by many investigators. Smith⁽²⁹⁾ showed the effect of several activators with strontium selenide phosphors. The maximum brightness was obtained, for example, with two parts strontium oxide to 100 parts strontium selenide. They also

used simultaneous addition of the sulfide and oxide ions and found that with increasing amounts of the oxide, the less sulfide was required to give maximum efficiency. The increasing of sulfide proportions caused a shift of the emission color to the red while the oxide in concentrations above 3% caused a rapid decrease of sensitivity.

IV-C. STIMULATION AND QUENCHING DIFFERENCES

The most marked differences between stimulation and quenching is the wave lengths affecting each. We have already spoken of the theories of Klasens-Schön and Rompe on quenching. Also, we discussed the stimulation as it was used in explanation on the simple model. However, an alternate hypothesis on the concept of the large complex emission centers in sulfide phosphors might provide a more satisfactory explanation of the differences between quenching and stimulation. Stimulation may consist of the absorption of radiation and the excitation of electrons into the upper levels of the center. From these levels, the electrons would make radiative transitions to their ground states. Quenching radiation, which is of higher quantum energy, may eject electrons into the conduction levels when they would be prone to capture in non-radiative centers. Overlap of quenching and stimulation spectra would be explained by the probability of thermal activation of the electrons excited from higher states of the emission centers into the conduction band and their behavior then as electrons ejected by quenching radiation. Such a process would be temperature dependent and would be revealed by a change in the relative configurations of the quenching and stimulation spectra in their overlapping region. This needs verification by experimentation.

IV-D. VARIATION IN DECAY

Next we shall see how the decay is affected with time. Fonda⁽³⁰⁾

suggests a simple monomolecular process for the zinc sulfide phosphors. However, his results lack the effect of infra-red radiation intensity on the rate of decay which would help test the theory. Urbach⁽⁷⁾, however, suggests that the decay processes are not simple as the exponential form of the decay is not general. Some explain it as a simple superposition of exponential decays. This would not necessarily be informative as any curve can be made up by proper choice of curves for the superpositioning. Ellickson and Parker⁽³¹⁾ suggest that the thickness of the phosphor be taken into consideration assuming that both stimulating and emitted light are absorbed in passing through a finite thickness of phosphor. But Urbach⁽³²⁾ does not agree. He measured exhaustion curves of layers sufficiently different in thickness to cause a brightness variation of one power of ten. The thinnest layer appeared equally bright whether it was viewed from the side of the incident stimulating light or from the opposite side. We should expect a strong difference in the shape of these exhaustion curves if absorption played an important part in the process. These experiments yielded, however, much the same shapes, in particular, the same slope.

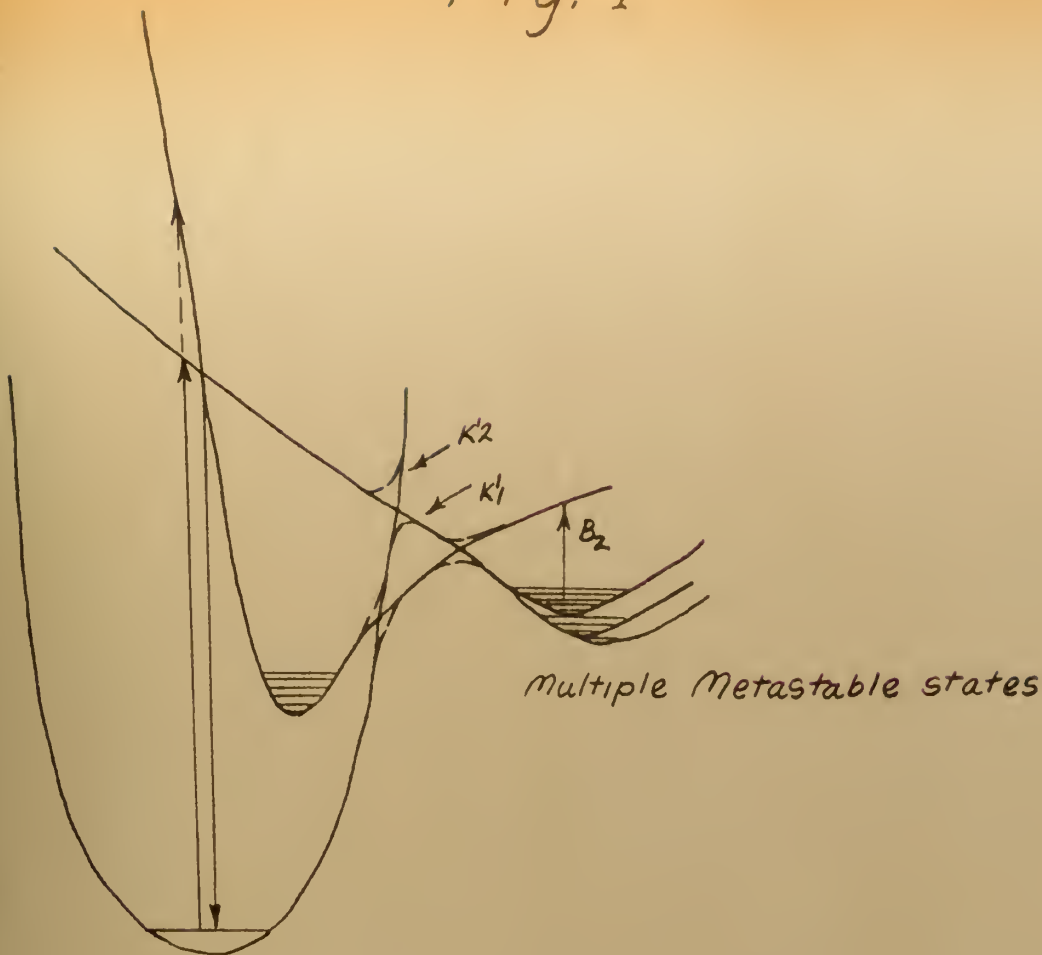
Variations of the decay rate are also caused by the effects of temperature. In the treatment of the diverse effects in the luminescence of ordinary phosphors by an analysis based on the configuration coordinate model, some of the correlations depend on rather small experimental effects. For example, the correlation between the heat of activation for metastable phosphorescence and the heat of activation for the rate-determining steps in the actual luminescence process depends on the relatively small decrease in luminescent efficiency with decreasing temperature. In fact, only a weighted average heat of activation is obtained because of the more frequent participation

of very shallow electron traps in the luminescent process.

With the infra-red-sensitive phosphors, in which there is the possibility of the optical transition B_2 from the metastable to the emitting state as shown in Figure 4, many of the effects that were small in the case of ordinary phosphors take on large values. For example, the depths of the electron traps are greater. For this reason not only is the phosphorescence very slow at ordinary temperatures in the absence of infra-red stimulation, but also, as predicted from the model, there is an extraordinarily large decrease in luminescent efficiency with decreasing temperature below the temperature of maximum efficiency. The data of Shrader⁽³³⁾ for the SrS:Sm:Eu phosphor demonstrates this effect. Because of the Franck-Condon principle and the shape of the potential energy curves of Figure 4, we should expect that the optical activation energy would be greater than the thermal activation energy. The latter should differ only slightly from the heat of activation because there is certainly very little volume change during the activation process. That the optical and thermal energies differ by a factor of almost five would indicate that shallow electron traps are active. This fact is verified by the complex character of the phosphorescence of the SrS:Sm:Eu phosphor.

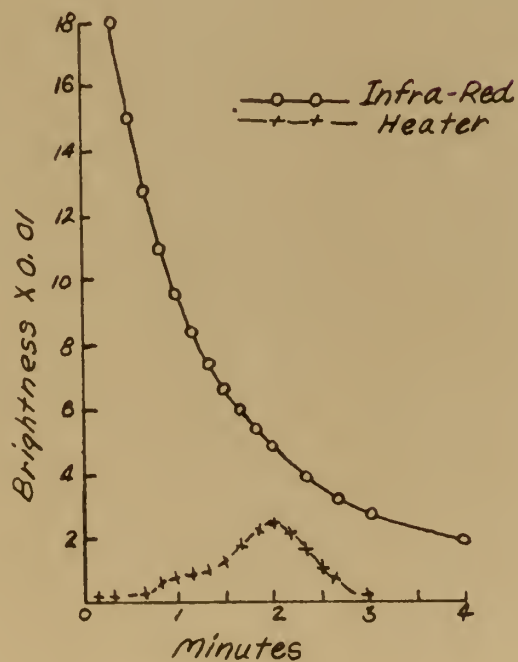
In the SrS:Sm:Eu phosphor, it is interesting to note that the most slowly decaying phosphorescence occurs at the temperature of maximum luminescent efficiency. The explanation is that at this temperature all the metastable levels are participating in the luminescent process to give the maximum efficiency, and the summation of the exponential afterglow contributions to the emission intensity approximates a slowly decaying t^{-1} phosphorescence⁽³⁴⁾. It might also be of interest to note the difference of the light sum obtained

Fig. 4



Configurational coordinator diagram for luminescence.

Fig. 5



Exhaustion of Sr S-Ce-Sm phosphor under infra-red and thermal stimulation.

from a single sample infra-red phosphor when it is heated and when it is irradiated with infra-red light⁽³⁵⁾. See Figure 5.

V. INFRA-RED PHOSPHOR DEVELOPMENT

The requirements of a good infra-red sensitive phosphor for use with stimulation are evident. The efficiency of conversion of infra-red into visible radiation must be high. The spontaneous emission (normal decay from original excitation called "background") should be low at the time of use. The spectrum of the stimulated emission must be favorable for scotopic vision. Sufficient energy should be stored to avoid the need for frequent re-excitation. High infra-red sensitivity should extend to sufficiently long wave-length to permit efficient elimination of visible light. Adequate excitation should be possible by convenient and inexpensive sources. Various other conditions of a more technical nature would also be required, depending upon its intended use.

A. WARTIME NEEDS

The task of finding these phosphors for immediate utilization became a big assignment during the late World War II. And during this period of frantic development, much was done on the technical side to fulfill the requirements stated above but the basic theories received little further attention.

It was during this period that a tremendous effort was exerted to perfect the bolometers⁽³⁶⁾, the devices for detecting or measuring small quantities of radiant or heat energy. Since then, there has been continuing work but at a much slower rate. More recently, Simpson⁽³⁷⁾ gives some new photoconducting cells for infra-red detection. Moss⁽³⁸⁾ explains some detection improvements and procedures as well as some theoretical limits of sensitivity of lead-salt-photo-conductive cells. These devices, however useful, are in need of further study and development. For example, the sniper scope works

very well, but the range is limited by the "scope". It would be desirable to have an instrument whose range was not limited by the technical limitations of the device itself. Some phosphor signal receivers used by the services are required to be charged and "aged" up to four hours before use. Others require radium for the initial excitation. Some have built-in radium sources that keep the phosphor in a constant state of excitation and need only a matter of seconds for aging. As you can see, all of these mentioned have serious handicaps for efficient field utilization⁽²⁴⁾.

B. PRODUCTION DIFFICULTIES

The alkali halide phosphors were dropped from serious consideration because of the necessity for radium excitation. Next, attention was turned to the sulfide phosphors as there was much information available on them due to the early work of Lenard on stimulation as well as quenching.

A large number of sulfide phosphors were prepared by the method of Lenard but none of these seemed to offer the desired solution. These that showed fair stimulation were particularly useless due to their bright spontaneous afterglow, that is, the stored energy dissipated too rapidly by phosphorescence. If this strong afterglow was allowed to dissipate by normal decay to a point necessary for utilization, then the efficiency was so low as to prevent its use.

Another method of suppression of afterglow proved to be more efficient. In the case of a strontium sulfide-bismuth phosphor, the excitation was carried out at the temperature of liquid air. Then the phosphor was allowed to warm up slightly during a short period of time, cooled again to temperature of liquid air, where it was used. In the case of a calcium sulfide-lead phosphor, excitation was carried out at room temperature and then immediately cooled to the temperature of dry ice and used at that temperature. These phosphors, stored cold, held their sensitivity for a few days by inhibiting

or slowing down their spontaneous emissions permitting a larger storage of light longer and also reduced background materially. These cooled phosphors allowed high sensitivities but it is readily seen to be a handicap when utilization requires a temperature other than the normal temperature of the surroundings. The handling of the coolants necessary and the prevention of moisture become tasks of major proportions.

Despite the early difficulty of reproducing the Lenard phosphors by his "recipe" and the fact that there were no rules to guide any search for new phosphors, some of the unknown details gradually began to be revealed.

Some calcium sulfide-samarium phosphors at room temperature attracted much attention by their rather strong red emission upon stimulation by infra-red light and by their relatively weak orange background. The sensitivity to stimulation seemed to vary strongly with the samarium sample used. Attempts were then made to eliminate the poisoning effects by obtaining very pure samarium. This did not help, however. The purest samples did not produce good sensitivity, whereas one containing considerable amounts of europium as well as gadolinium yielded remarkable stimulability. Thereupon attempts were made to prepare phosphors activated by either of these elements. It was not until some very pure europium (prepared by the late Professor Herbert N. McCoy and presented as a gift by Professor Karl Przibram) was utilized, that it became clear that only a combination of at least two rare earths were necessary for the production of strong infra-red sensitivity.

After resumption of this work it soon became known that there was a large class of phosphors in which the presence of two activators produced a sensitivity to stimulation which was not obtained by one activator alone. This was also true but in a different manner in the zinc sulfide phosphors.

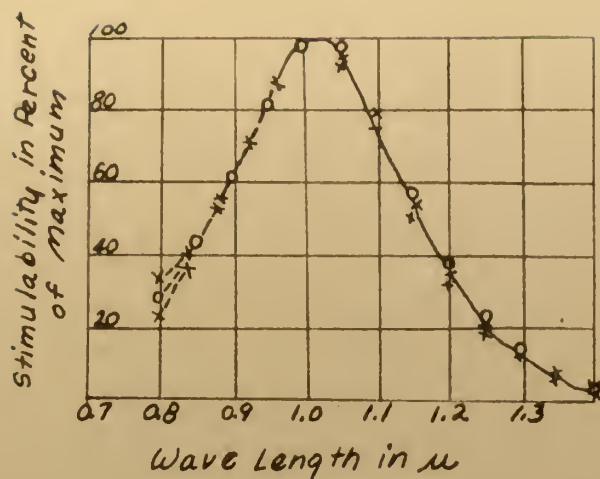
With the necessity of two activators, some kind of interaction was not unexpected. It was known that certain elements act as activators in the

same bases and as poisoners in others. Other cases of interaction of activators which have been described are the sensitization of excitation and the exaggerated phosphorescence of certain silicate phosphors. The existence of conduction bands and the possibility of "exciton"-diffusion in the modern theory of solids rather lead one to expect such interaction phenomena. In fact, such interactions seem to be the rule rather than the exception. The various functions of activators - their contribution to absorption and excitation, the light storage caused by them, and the spectral characteristics of emission - may be shared by or distributed among, various activators simultaneously present in the same phosphor.

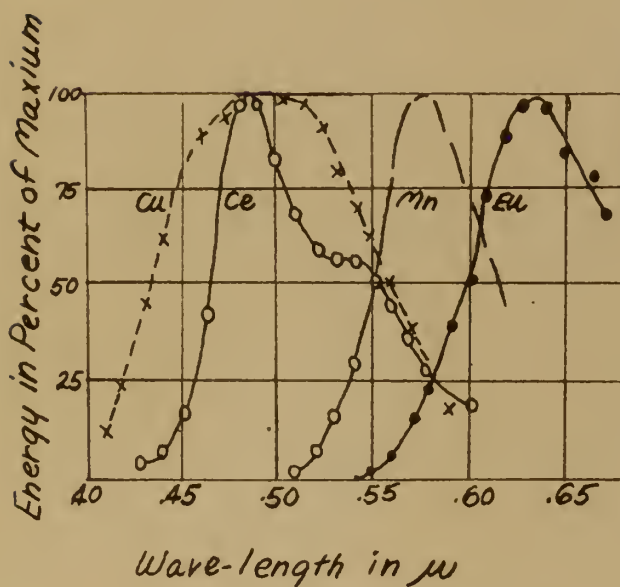
A heretofore unknown pattern of the infra-red sensitization of alkaline earth sulfide phosphors is discussed. One activator - the dominant activator - whose presence produces the characteristic emission which can be sensitized to stimulation by the presence of another - auxiliary - activator, which in turn determines the spectral distribution of sensitivity to stimulation. For example, four different activators in strontium sulfide phosphors prepared with fluxes (usually calcium fluoride or lithium fluoride) and heating cycles found empirically to be favorable for the development of these emissions. These are shown in Figure 6. None of these phosphors shows a pronounced stimulation by infra-red light but by preparing these same phosphors with an addition of samarium they all became sensitive to infra-red stimulation, the stimulation spectrum centered around 1 micron.

Figure 6 (a) shows phosphors with vastly different concentration ratios of the activators. In spite of the differences in samarium concentrations, its relation to the concentration on the dominant activator, the stimulation spectra of the three phosphors are almost identical. The samarium is

Fig. 6



(a). Spectral distribution of stimulation in strontium sulfide phosphors with various dominant activators and samarium as an auxiliary activator. \circ : europium-samarium, $+$: manganese-samarium. \times : cerium-samarium.



(b). Emission spectra of strontium sulfide phosphors activated with copper, cerium, manganese, and europium, respectively.

responsible for the stimulation band around 1 micron, however all these phosphors emit only spectra shown in Figure 6 (b) upon stimulation. There are many other examples showing this relationship between dominant and auxiliary activators⁽³⁹⁾.

With some phosphors the auxiliary activators produce some stimulation of its own emission. But in most cases the extinction is preponderantly a quite conspicuous quenching (at least at room temperature).

In the investigation of the poisoning effects of activators it was found that in the alkaline earth sulfide group of phosphors very small amounts of samarium suffice to diminish the brightness of the afterglow caused by manganese or copper by several orders of magnitude. However, the phosphor was not poisoned and the light emission was not really suppressed but merely slowed down, the total amount of stored light is increased (revealed by heating or stimulation). In some cases the suppression of afterglow is mutual. In the europium-samarium combination, the addition of relatively small amounts of europium reduces the samarium afterglow considerably even in the phosphor is excited with a wave length which produces strong afterglow in a pure samarium phosphor. A real reduction of the total emission of the auxiliary activator seems to occur in such cases.

Samarium seems to be the most important auxiliary activator but there are many more. A few possible combinations are presented here:

Dominant Activators	Activator pairs			Auxiliary activators				
	Sm	Bi	Sn	Fe	V	Ni	Pb	Ag
Eu	+	+	+	+			+	?
Ce	+	+	+	+	+	+	+	?
Mn	+	+	+	+		+		
Cu	+	+	+	+	+	+		

Three groups of infra-red phosphors are given in the appendix. Also in the appendix are the variations of effects among different preparations as well as some data demonstrating some of the phenomena previously discussed.

CONCLUSION

There seems to be no rule concerning activators except that one must use extreme caution in preparation of the activated phosphors. Frequently, very minute traces of one activator have profound influences on the behavior of the other. Traces in the quantity of 10^{-13} gram of activator to one gram of base is sufficient to spoil some materials.

The sensitization of stimulation by auxiliary activators was a boon to development of infra-red phosphors. Several of the most desirable properties, increased light storage, lower afterglow, and infra-red sensitivity were produced by auxiliary activator. And due to the combinations of auxiliary with dominant activators, we have a choice of emission spectra with a given stimulation spectrum.

Quite a bit is known about the infra-red effects of phosphors but not enough; however, most of the problems are on the general theories of luminescence. Different experimental observations indicate different theories, each of which could possibly be correct for the specific phosphors examined, however, not correct generally. For example, some phosphors decay in a monomolecular manner and some have a more or less bimolecular decay. In other words, the luminescent materials studied exhibit complexities and anomalies which cannot be interpreted in a simple way. There have been some irregularities observed that imply that the existing theories must be generalized and made more complicated. On the other hand, some of the complexities which have been stressed have other origins and have little to do with the validity of existing theories.

For progress to be made in the fundamental interpretation of the mechanism of luminescence, experimenters must not assign too high degree of importance to results but must be willing to simplify and refine the experi-

mental conditions in such a way as to eliminate extraneous complicating factors and turn out a large volume of data. As we know, the band theory does not explain the various properties of some of the more complicated phosphors.

The facts known today about excitation waves and the excited states of impurity centers have been won with considerable effort and should not be discarded lightly on the basis of results obtained from a highly complex material. There are other fields of solid state physics in which these same principles have been used with considerable success.

In spite of the practical interest in the field of infra-red sensitive phosphors, real development will come by research carried out painstakingly on simple materials under conditions where a high degree of reproducibility is possible, even though no practical use is foreseen.

APPENDIX

SOME PREPARED INFRA-RED PHOSPHORS

First Infra-Red Phosphor

In 1934 Joseph Kunz and others started work on infra-red detection and on infra-red photography with the aid of stimulation in contrast to the extinction uses previously. This was started when a phosphor was found with a weak afterglow but a relatively large light storage and fairly high stimulating sensitivity. This was radium excited potassium chloride. This type of phosphor was abandoned when the development of sulfide phosphors was begun.

A. Lanthanum Oxysulfide Phosphor

John J. Pitha et al⁽⁴⁰⁾, give some activators which give infra-red sensitive phosphors with lanthanum oxysulfide. Indium and lead were tested using concentrations varying from 50 to 500 parts per million of lead and 50 to 2000 parts per million of indium. The most sensitive were those containing about 200 parts per million of lead to about 400 parts per million of indium. None of the phosphors were as sensitive as strontium sulfides activated with samarium and europium.

The lanthanum oxysulfide phosphors differ from those of the alkaline earth sulfides and selenides in that they do not appear to be affected adversely by grinding. On the other hand, no suitable flux was found for these phosphors. Several phosphates, fluorides, borates, and sulfates were used but only to the detriment of the infra-red sensitivity. The pairs of activators found to give infra-red stimulated phosphors in approximate order of sensitivity is given in Table I.

TABLE I.

Activators which give infra-red sensitive phosphors with $\text{La}_2\text{O}_2\text{S}$.

Activators	Color for phosphorescence and stimulated light
Pb In	Green
Pb Eu	Orange
Bi Eu	Orange
Sm Eu	Orange
Gd Eu	Orange
In Eu	Orange
Bi In	Green

B. Strontium Base Phosphors

Stripp and Ward⁽⁴¹⁾ showed that impurities other than heavy metals have a profound effect on the behavior of phosphors. The strontium sulfide-samarium, europium phosphor fluxed with lithium fluoride and with strontium chloride was shown to be affected by the addition of small quantities of strontium oxide. The presence of lithium fluoride or of calcium ions increases the tolerance of the phosphor toward oxide.

The dependence of the brightness of the phosphor upon the concentration of samarium and europium, using strontium chloride as flux, was determined.

Table II⁽²⁹⁾ gives some effects of activator pairs which produce infra-red-sensitive phosphors with Sr Se. The mixture 100 SrSe + 5SrS(0.020Sm0.020Eu) ($6\text{-SrSO}_4, 6\text{CaF}_2$) was found to give a produce resembling that obtained by use of strontium sulfite. We shall call it a strontium selenide phosphor, SrSe (Sm, Eu) even though small amounts of sulfide or other impurities have been added.

TABLE II.

Activators which produce infra-red sensitive phosphors with SrSe.

Activator pair	Fluorescence	Phosphorescence	Infra-red activity	Color of emission
Ei-Mn	Yellow	Yellow	Very weak	-
Bi-Pb	Orange	Orange	Very weak	-
Cu-Bi	Yellow-Green	Orange-Yellow	Weak	Green

TABLE II., Continued

Activator pair	Fluorescence	Phosphorescence	Infra-red activity	Color of emission
Cu-Pb	Blue-green	Green	Weak	Green
Eu-Pb	Orange	Blue	Weak	Orange
Eu-Bi	Yellow	Yellow	Strong	Yellow
Sm-Bi	None	None	Weak	Green

The stimulation spectrum given in Figure 7 (a) represents the sensitivity of the 100 SrSe + 5 SrS(0.02Sm,0.02Eu)(6CaF₂,6SrSO₄) phosphor to the infra-red spectrum in terms of its brightness response, measured with a Beckman quartz spectrophotometer. Figure 7 (b) shows the emission spectrum of the stimulation phosphor, obtained by photographing the spectrum with a Hilger Constant Deviation Spectrometer and analyzing the spectrograms with a Leeds and Northrup recording microphotometer. The peaks of the stimulation and emission bands lie at 0.93 and 0.569 micron.

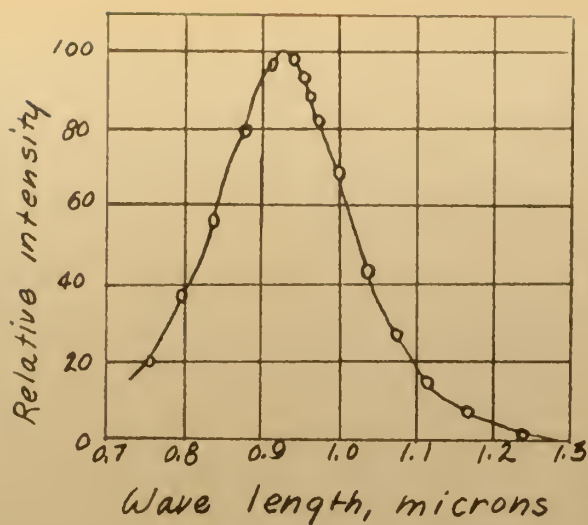
Samples of the selenide phosphor 100SrSe + X SrS(0.023Sm,0.020Eu)(7.5SrSO₄,7.5CaFe) and 100SrSe + YSrO(0.023Sm,0.020Eu)(7.5SrSO₄,7.5CaF₂) were prepared in which X varied from 0-5 and Y varied from 0-8. The relative brightness is given in Table III. The decrease of intensity of emission with more than 3 parts strontium sulfide may be partly due to the shift in color of emission toward the red, as the photocell (RCA 931A) used in these observations is less sensitive in this region of the spectrum.

TABLE III.

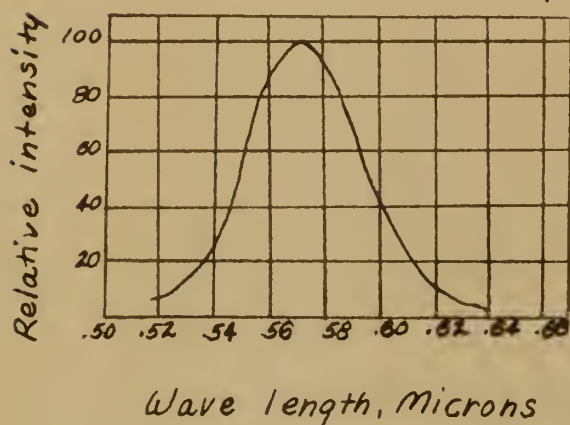
Influence of oxide and sulfide ions upon the brightness of strontium selenide phosphors

(a) SrS	0	1	2	3	44	5	6	8
Relative Brightness	70	78	102	140	100	70	75	67
(b) SrO	0	1	2	3	5			
Relative Brightness	60	84	112	94	42			

Fig. 7



(a). Stimulation spectrum of 100SrSe - 5Srs - (0.020Sm, 0.020Eu)(6SrSO₄, 6CaF₂).



(b). Emission spectrum of 100SrSe - 5SrS(0.020Sm, 0.020Eu)(6SrSO₄, 6CaF₂).

A series of phosphors $100 \text{ Sr Se} + X \text{ SrO} + Y \text{ SrS}(0.023 \text{ Sm}, 0.020 \text{ Eu})$ ($7.5 \text{ Sr SO}_4, 7.5 \text{ Ca F}_2$) were prepared with $X = 0$ to 2 and $Y = 0$ to 4 . The results given in Table IV indicate that with increasing amounts of oxide, less sulfide is required to give the phosphor its maximum efficiency.

TABLE IV.

Influence of simultaneous addition of sulfide and oxide ions upon the relative brightness of the strontium selenide phosphors.

Srs		0	1	2	3	4
SrO	0	70	78	114	140	117
	1	120	125	128	120	
	2	123	136	130		

The reproducibility of the brightness values are for any sample within five percent. A reasonable correlation among samples in a particular series usually was obtained, but wide variations were frequently found from one series to another. The discrepancies were attributed to: (a) different strontium selenide preparations, (b) different atmospheric conditions during the mixing of samples, (c) slight variations in firing conditions, and (d) the oxidation of strontium selenide by sulfate ion at the surface of the samples.

It seemed reasonable to suppose that better control of the final composition of the phosphors would result from the use of non-oxidizing fluxes. A mixture of $100 \text{ SrSe} + 4\text{SrS} + 3\text{SrO}(0.023\text{Sm}, 0.02\text{Eu})(5\text{LiF}, 6\text{CaF}_2)$ was heated at 1050 degrees in a stream of oxygen-free nitrogen for periods of time varying from 15 minutes to two hours. The results of this is given in Table V. It is noted that the brightness and phosphorescence change very little after thirty minutes of heating.

TABLE V.

Effect of duration of heating on luminescent properties using a non-oxidizing flux.

Time (minutes)	Phosphorescence at 30 seconds after excitation	Relative brightness under infra-red stimulation
15	210	10600
30	420	14200
60	420	13900
120	460	12400

While elimination of sulfate ion from the flux makes the heating time less critical, erratic results were still obtained when different strontium selenide preparations were used. For example, two series of mixtures of $100\text{SrSe} + \text{XSrO}$ ($0.023\text{Sm}, 0.020\text{Eu}$) (5LiF) prepared from different batches of strontium selenide.

The results are very different in some respects but both series show a maximum in brightness at about 3 parts strontium oxide. See Table VI for the results.

The only exceptionally striking phosphor from the calcium selenide samples is the $100(\text{CaSe}, \text{CaO})(0.020\text{Sm}, 0.020\text{Eu})(6\text{CaSO}_4, 6\text{CaF}_2)$. The stimulation spectrum has a maximum at 1.03 microns. Its emission color is yellow-orange with the peak of the emission band being approximately 0.585 microns. From some X-ray studies of selenide phosphors containing calcium we might infer that the calcium ion tends to form a separate phase with oxide.

TABLE VI.

Effect of added oxide upon brightness and phosphorescence of $\text{SrSe} - \text{SrO}(0.023\text{Sm}, 0.020\text{Eu})(5\text{LiF})$

Series	X(SrO)	Phosphorescence at 30 seconds after excitation	Relative brightness under infra-red stimulation
1	0	not detectable	470
	1	72	600
	2	560	4470
	3	2490	6510
	4	5300	3420

TABLE VI - Continued

Series	X(SrO)	Phosphorescence at 30 seconds after excitation	Relative brightness under infra-red stimulation
2	0	500	6000
	1	200	5400
	2	300	7600
	3	400	11400
	4	500	5900

C. ALKALINE EARTH SULFIDE AND SELENIDE PHOSPHORS

Pure Strontium Sulfide was prepared by complete reduction of strontium sulfate with hydrogen. Various physical compositions and preparations were used. Bright phosphors were obtained with strontium sulfide activated with cerium and samarium using various fluxing agents such as calcium fluoride and lithium fluoride. From the results of this, it appears obvious that an important function of the sulfate ion is to give a sufficient quantity of liquid phase at a convenient firing temperature. Presumably, the liquid serves as a recrystallization medium for the base material, and during the recrystallization the activator ions are incorporated in the lattice of the base material. Some characteristics emission colors of the simple phosphors are listed in Table VII.

TABLE VII

Emission of Individual Sulfide and Selenide Phosphors

Base Material	Activators	Exciting Light	Emission
SrS	Eu Sm	Blue-green	Orange-red
SrS	Ce Sm	Ultra violet or Radium	Green: (background green and orange).
SrSe	Eu Sm	Blue-green or ultra violet	Yellow
CaS	Eu Sm	-	Red
CaSe	Eu Sm	-	Orange-red

The preparation of infra-red phosphors of the alkaline earth phosphors of the alkaline earth sulfides and selenides by the Lenard method is shown

to involve a complicated interaction of the base material and the flux. However fluxes may not be essential to the formation of all alkaline earth sulfides, infra-red sensitive phosphors as a bright phosphor $\text{SrS}(\text{SmEu})$ is prepared without the addition of a flux. (42)

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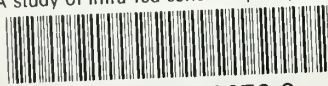
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